LIGHT ABSORPTION IN NO_3^- ION IN STATE OF SOLUTION
PART IV.—EFFECT OF DILUTION

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ABSTRACT. 200 $m\mu$ band which has been assigned to an allowed $\pi \longrightarrow \pi^*$ transition of nitrate ion, exhibits blue shift with progressive dilution in state of aqueous solution. This shift has been attributed to hydrogen bonding which occurs at the oxygen atoms decreasing the electron density around oxygen atoms in the nitrate ion.

INTRODUCTION

In part II of the present series of the papers (Mookherji and Tandon, 1965), a systematic study of the energy, band-width, intensity and structure of the 200mμ band at concentrations $\sim 10^{-5}M$ of nitrate ion has been reported. Evidences have been cited for its assignment to an allowed $\pi \rightarrow \pi^*$ transition.

Solvents are known to influence (McConnell, 1952; Strickler, 1961; Strickler and Kasha, 1961) the position of the bands of the solute. Study of the $n \rightarrow \pi^*$ transitions of the organic (Borawoy, 1939; Kasha, 1950; Coggeshall and Pozefsky, 1951) and inorganic molecules (McConnell, 1952; Strickler, 1951; Strickler and Kasha, 1961; Meyerstein and Treinin, 1961) reveals a blue shift of the bands in increasing polarity solvents. Water is a strongly polar solvent abounding in hydrogen bonding. In state of aqueous solution the hydrogen bonding increases with dilution. Consequently, the spectral shift of the solute is expected to increase with progressive dilution. Since π-orbitals in nitrate ion are similarly situated (Mookherji and Tandon, 1965) as n-orbitals, $\pi \rightarrow \pi^*$ transitions in this ion are expected to exhibit band shifts similar to that of $n \rightarrow \pi^*$ transitions.

The present communication reports the study of the 200mμ band of nitrate ion, which has been assigned to $\pi \rightarrow \pi^*$ transition (Mookherji and Tandon, 1962, 1965), at different concentrations($\sim 10^{-1}M$ to $10^{-4}M$) in state of aqueous solution with UVISPEK sepctrophotometer. The results have been discussed in the light of Griffiths and Symons (1960) and Strickler (1961).

EXPERIMENTAL AND RESULTS

Chemicals used were of Merk's analytical reagent quality. Triple distilled water was used for making solutions.

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The measurements were carried out with Hilger's UVISPEK spectrophotometer by the method described earlier (1961), scanning the spectrum at an interval of 2.5 Å on five nitrates-$LiNO_3$, $NaNO_3$, KNO_3, NH_4NO_3 and $AgNO_3$, at different concentrations (10^{-1} to $10^{-4}M$) in state of aqueous solution. Since the nature of absorption in all these salts was same, to avoid repetition, the absorption curves of lithium nitrate are given in Fig. 1.

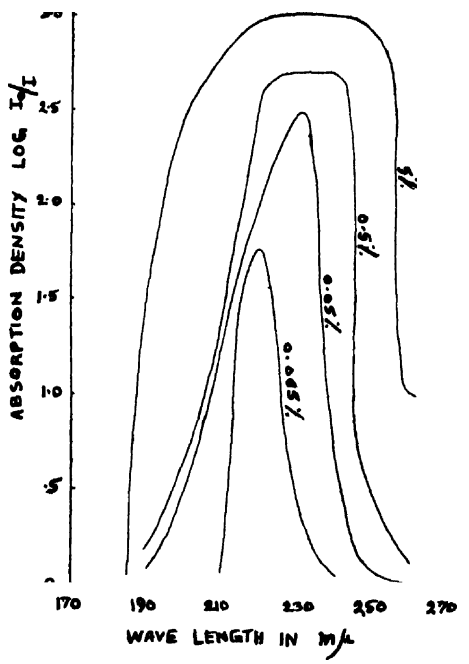

Fig. 1. Absorption curves showing blue shift of 200 *mu* band of lithium nitrate with progressive dilution in state of aqueous solution.

The measurements centred round about 25°C. No observable change in the position of the absroption maxima was noticed for small room temperature variations.

DISCUSSION

Close study of Fig. 1. reveals a blue shift $\sim 10^3$ cm^{-1} in going from 10^{-1}M to 10^{-4}M concentration of aqueous solution of nitrates. At high concentrations the absorption maxima are flat and become sharp with dilution.

To explain similar influence of environment several models (Griffiths and Symons, 1960) have been used (Cleaver *et al*, 1961; Shimoji, 1961). In "expanded model" (Platzman and Franck, 1964) the orbital of the excited electron is regarded as invading surrounding medium quite deeply whereas in "confined model" (Smith and Symons, 1958), the orbitals of the excited electron are confined within the

nearest neighbour shell. Simple calculations of the retaining force on the excited electron, representing it by an infinite square well potential having spherical and symmetry and radius R_0, show that R_0 comes out to be much larger than the sum of the radii of the cation and anion in complete disagreement with the case of iodide ion (Smith and Symons, 1958), which is known to give electron transfer spectra. This coupled with the study of the effects (Strickler, 1961) of temperature and solvent, suggest that the observed spectrum of the nitrate ion is not due to electron transfer but is due to the electron transitions localized on the ion itself. Consequently, the above described modes of influence of environment, which are meant for the electron transfer spectra, cannot be used in the case of nitrate ion.

Nitrate ion is known to have planar structure with oxygen atoms at the corners of an equilateral triangle and the nitrogen at the centre, having D_3 symmetry and positive charge on nitrogen atom in close proximity to the negative charge on the nitrate ion (Janz and Mikawa, 1960). LCAO-MO treatment of the ion shows that π-orbitals like n-orbitals are localized on the oxygen atoms whereas π -orbitals on the nitrogen atom in the nitrate ion. Hence $\pi \rightarrow \pi^*$ transitions also remove an electron from an antibonding π-orbital and places it in a strongly antibonding π^*-orbital. This results in a decrease in electron density in the region where π-orbital was located. A hydrogen bond formed with the oxygen atom having π-orbital, places a positive charge near that orbital, making it more difficult to remove the electron. This causes the increase in the energy of $\pi \rightarrow u^*$ transition, shifting the band to higher ferequencies. As hydrogen bonding increases with dilution, the blue shift of the band should also increase with progressive dilution. This is what has been observed

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